

## Supporting information:

# The electronic properties tuned by the synergy of polaron and d-orbital in Co-Sn co-intercalated $\alpha$ -MoO<sub>3</sub> system

*Xin Xu, † Haojie Lai, † Yufan Xia, † Tian Luo, † Yuxuan Chen, □ Siyuan Wang, †, ‡ Ke Chen, † Xin Wang, □ Tingting Shi, \*, †, ‡ Weiguang Xie, \*, †, ‡ Pengyi Liu, \*, †, ‡*

† Siyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics, Jinan University, Guangzhou, Guangdong 510632, China

‡ Guangzhou Key Laboratory of Vacuum Coating Technologies and New Energy Materials, Guangzhou, Guangdong 510632, China

□ National Center for International Research on Green Optoelectronics, South China Normal University, Guangzhou, Guangdong 510006, China.

## Corresponding Author

\*E-mail: [ttshi@email.jnu.edu.cn](mailto:ttshi@email.jnu.edu.cn)

\*E-mail: [wgxie@email.jnu.edu.cn](mailto:wgxie@email.jnu.edu.cn)

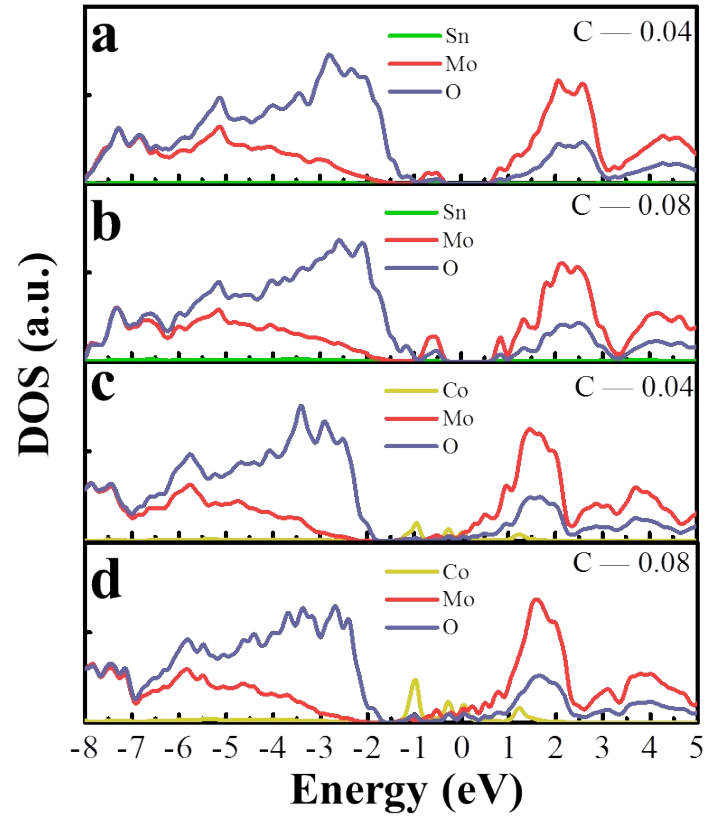
\*E-mail: [tlpy@jnu.edu.cn](mailto:tlpy@jnu.edu.cn)

## COMPUTATIONAL METHODS

In this paper, we perform first-principles density functional theory calculation utilizing the Vienna Ab initio Simulation Package (VASP)<sup>1</sup> code with the projector augmented wave method (PAW)<sup>2</sup>. The generalized gradient approximation (GGA)<sup>3</sup> of Perdew-Burke-Ernzerhof (PBE) was applied for electron exchange and correlation. For the defect calculations,  $2 \times 1 \times 3$  supercells were chosen, which contained 96 atoms (24 Mo atoms, 72 O atoms). The Kohn-Sham equation is solved by a plane wave basis set with a cutoff energy of 400 eV, and the Brillouin zone samples a  $4 \times 2 \times 3$  mesh centered at  $\Gamma$  point. Atoms are fully relaxed until the Hellmann-Feynman forces on them are within 0.05 eV/Å. To get more accurate electronic properties related to the localized states, we also use the GGA+U method<sup>4</sup> correction in our calculation. The U value was set to 6.3 eV, which is consistent with the previous study.<sup>5</sup> Moreover, the standard Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional with standardized parameter ( $\mu=0.2 \text{ \AA}^{-1}$  and  $\alpha=0.25$ ) is also considered for get more accurate band gap which is in line with the experimental values.

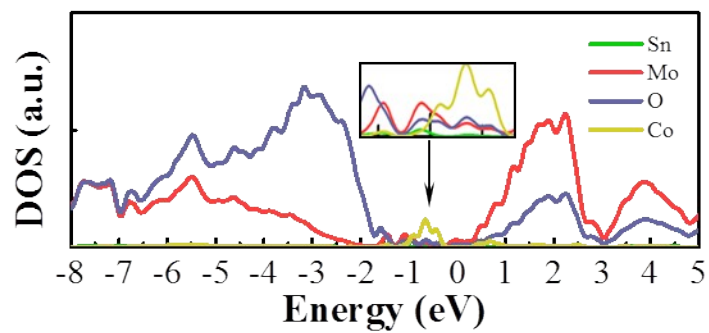
To synthesize  $\alpha$ -MoO<sub>3</sub> nanosheets with good quality, we used muffle furnace as heating platform and chose Mo foil as molybdenum source. First of all, the muffle furnace was heated to 580 °C to maintain the stability. The Mo foil was placed on the quartz sheet and put into the muffle furnace to preheat for 2-3h, so that the surface of Mo foil was oxidized to form  $\alpha$ -MoO<sub>3</sub> crystal. Then we took it out and put it on the surface of SiO<sub>2</sub> substrate for making the good contact between the Mo foil crystal surface and the substrate. After 2-5 minutes treatment in muffle furnace, we finally obtained batches of suitable  $\alpha$ -MoO<sub>3</sub> nanosheet.

Based on the well-prepared  $\alpha$ -MoO<sub>3</sub> nanosheets, we started the intercalation of different metals. Herein, our experiments employed a two-step intercalation method. We firstly selected Sn atoms for the intercalation. At the beginning, we weighed 0.75g tartaric acid and mixed it into 50mL deionized water, and stirred them together to dissolve the acid. Then 0.1g SnCl<sub>2</sub> was added in the mixture and we continue to stir them until the solution become absolutely clear. When the solution was prepared appropriately, the  $\alpha$ -MoO<sub>3</sub> nanosheets could be placed into the solution and then was heated at 60 ° C in a water bath for 10 minutes to obtain  $\alpha$ -MoO<sub>3</sub> nanosheets partially intercalated with Sn. Subsequently, we started the secondary intercalation of Co ions. 0.1g cobalt sulfate powder was placed into 60ml deionized water using ultrasonic oscillation for getting the well mixed solution, which was finally added dropwise on the surface of the Sn-MoO<sub>3</sub> nanosheets. To get the intercalated nanosheet, three-dimensional console was used to interact with the intercalation area of the MoO<sub>3</sub> by controlling the contact between the Zn needle and the nanosheet. At first, the contact site began to be embed and impelled along the [001] direction. When it was impelled into the middle region of  $\alpha$ -MoO<sub>3</sub>, the Zn needle was lifted to finalized the contact with the sample which could be washed in the absolute ethanol to obtain Co-Sn co-intercalated MoO<sub>3</sub> and Co-MoO<sub>3</sub> nanosheets.

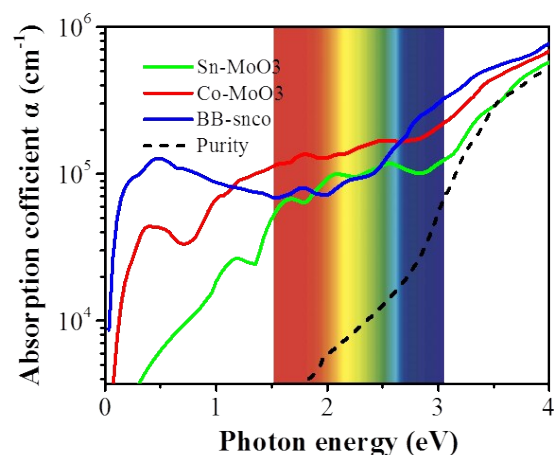


**Figure S1** The DOS of Sn and Co intercalated  $\alpha$ - $\text{MoO}_3$  at 0.04/0.08 concentration in site C.

The doping concentration is defined by the ratio of impurity to Mo atomic number.

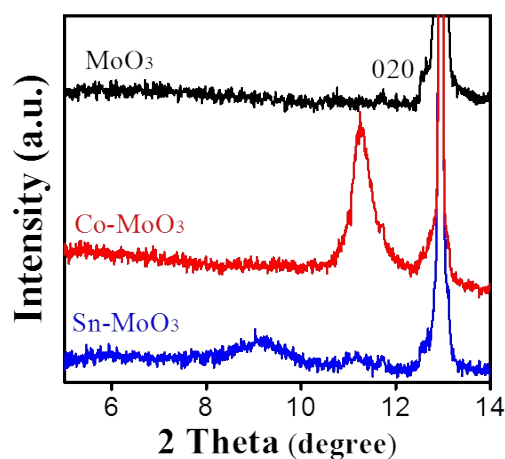


**Figure S2** The DOS of Sn-Co co-doped  $\alpha$ - $\text{MoO}_3$  system. Co and Sn were intercalated in site B simultaneously at a concentration of 0.04.



**Figure S3** The optical absorption coefficient spectra of Sn-MoO<sub>3</sub>, Co-MoO<sub>3</sub>, Sn-Co co-MoO<sub>3</sub> calculated by GGA+U method.

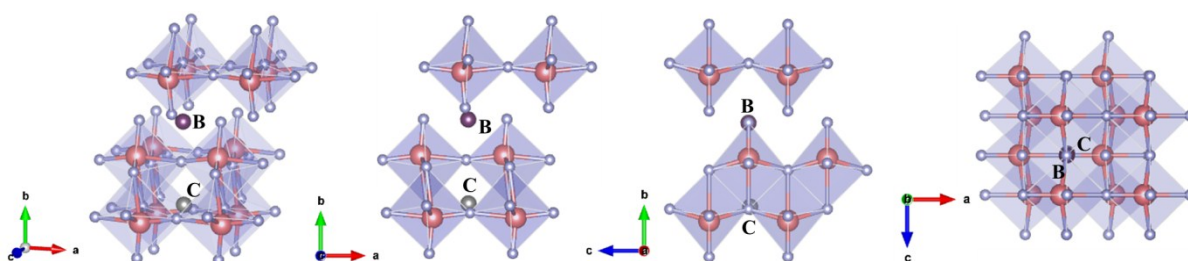
The optical absorption of co-doped systems emerge the most superior in long wavelengths of visible light, as well as the ultraviolet and infrared regions. Therefore the optical absorption properties are certainly promoted (**Figure S3**).



**Figure S4** XRD pattern of MoO<sub>3</sub>, Co-MoO<sub>3</sub> and Sn-MoO<sub>3</sub> nanodevice.

In order to verify that the atoms were indeed intercalated into the  $\alpha$ -MoO<sub>3</sub> crystals, we performed XRD tests on the nanosheets. As we can see in Figure S4, the intrinsic  $\alpha$ -MoO<sub>3</sub> has a distinct diffraction peak at  $13.02^\circ$ , which corresponds to the (020) plane (JCPDS: 05-0508) of  $\alpha$ -MoO<sub>3</sub>. Due to the expansion between layers at different degrees caused by the intercalation

of Co and Sn, some new peaks were observed at  $11.25^\circ$  and  $9.11^\circ$ , respectively. According to Bragg diffraction, the spacing distance of the (010) planes increased from  $13.95\text{\AA}$  to  $15.78\text{\AA}$  and  $19.51\text{\AA}$ , correspondingly. Since the nanosheets were intercalated partially, the eigen-peaks were still be observed. It was concluded that the Sn and Co atoms had been proved to be inserted into the  $\alpha\text{-MoO}_3$  nanosheets successfully from XRD pattern, which is also consistent with the Raman results. Furthermore, the local lattice change of Sn intercalated  $\alpha\text{-MoO}_3$  is bigger than that of Co intercalated system due to bigger atomic size. However, the concentration of Co intercalation is expected larger than the one of Sn intercalation because the different occupied sites were observed in Co intercalated system using Raman spectrum and DFT calculations.



**Figure S5** Intercalation sites B and C from different view angle.

B site is a symmetrical point located between the intra-layers, and is adjacent to the four terminal O atoms. C site is also a symmetrical point located in the inner-layers. It is adjacent to the five O atoms: three two-coordinated O atoms and two three-coordinated O atoms.

**Table S1** The total energy of impurity systems in A, B or C doping sites. The number represent the number of doped atoms in  $2\times 1\times 3$  supercells.

Total Energy/eV	Sn	Co
A	-612.490	-615.517
B	-912.971	-615.923
C	-612.366	-615.556
BB	-616.317	-622.398
CC	-614.700	-621.050
3B	-620.820	-628.643
3C	-617.921	-626.843

Doping site A and C with negligible small energy difference were found to be very similar. After doping the atoms at A, C position with atomic concentration 0.04, the energy difference of two doped systems is only 1.3 meV/atom. (Table S1) In addition, considering the periodic structure and symmetric properties of the crystals, A and C positions actually should have semblable doped properties when the lattice was completely relaxed. Therefore, these two positions are treated equivalently and the most stable doping B site was also selected in our calculation. Meanwhile, we find both B-site Sn and Co doping systems with same dopant concentration have the lowest total energies.

**Table S2** The total energy of Sn-Co co-doped  $2 \times 1 \times 3$  supercells. The first of the letters refers to where Sn is inserted and the second to where Co is inserted.

Site-SnCo	CB	BC	CC	BB
Energy/eV	-618.316	-618.631	-617.836	-619.072

From the total energy of the system, the co-doped system is minimum energy state when both foreign substances are doped in site B at the same time (see Table S2). As shown in Figure S2, the extended states in forbidden band are also primarily introduced by the 3d orbital of Co atoms, and a small part of impurity states that located nearby the CBM associated with small polaron. The synergy of the Co-3d states and polaron composed of lattice distortion and electronic extends the gap states across the forbidden gap, which can potentially enhanced the electronic conductivity, and even stronger than single atomic doping system.

## REFERENCES

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